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ION BEAM-ASSISTED PULSED LASER DEPOSITION FROM A PRE-SYNTHESIZED TI_3SIC_2 MAX-PHASE TARGET

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ABSTRACT

Pulsed laser deposition was used to grow thin films from a pre-synthesized Ti_3SiC_2 MAX-phase formulated ablation target on Si(100), MgO(100) and stainless steel substrates with and without a 200 V argon ion beam directed at the substrate surface during deposition. The depositions were carried out in a substrate temperature range from room temperature to 650 ˚C at a chamber pressure of 10^{-5} Pa without ion beam and at 10^{-2} Pa Ar background pressure when the ion beam was applied. The properties of the films have been investigated by glow discharge optical emission spectroscopy (GDOES) for film thickness and stoichiometric composition, X-ray diffraction for the crystallinity of the films and X-ray photoelectron spectroscopy (XPS) at the Ti 2p, Si 2p and C 1s core levels. Additionally, film hardness measurements were carried out by nanoindentation. X-ray diffraction measurements for all samples show no clear signs of the MAX phase Ti_3SiC_2, but only reflections of crystalline TiC. XPS measurements indicate the presence of pure titanium and silicon, both carbides TiC and SiC as well as substoichiometric oxides of titanium TiO_x and silicon SiO_x. GDOES measurements show that the films do not represent the desired stoichiometric Ti_3SiC_2 composition. Instead, the silicon content is decreased to about 11 at.% and below and a quite high oxygen content of about 7 at.% and more is observed. Obviously, silicon is oxidized by the residual oxygen during deposition and partially lost due to the formation of volatile SiO.

Keywords **–** MAX Phases, pulsed laser deposition, thin films, ion beam-assisted deposition, glow discharge optical emission spectroscopy (GDOES), X-ray diffraction (XRD), nanoindentation, X-ray photoelectron spectroscopy (XPS)

1. INTRODUCTION

$M_{n+1}AX_n$ (**MAX**) phases are a group of ternary carbides or nitrides with **M** being an early transition metal (mainly of the groups IVB and VB), **A** being an A group element (mostly IIIA and IVA) and **X** being either carbon or nitrogen. The prototypic compound Ti_3SiC_2 had already been synthesized in the 1960s [1], but not until 1996 its remarkable properties have been discovered [2]. MAX phases combine metallic properties such as good electrical and thermal conductivity with ceramic properties like thermal stability and resistance against oxidation [3]. These properties give rise to a potential application of MAX phases in thin films – for instance as wear and corrosion resistant coatings of electrical contacts. The growth of crystalline MAX phase thin films however is not trivial. The deposition of such films by magnetron sputtering has been reported [4-6]. One work concerning the pulsed laser deposition of MAX phase thin films has been published by Hu et al. [7] but was argued over in the scientific community [8-10].

In this paper, the growth of Ti/Si/C thin films from a pre-synthesized MAX phase Ti_3SiC_2 ablation target by pulsed laser deposition (PLD) is reported. The stoichiometric compositions of the films, the formation of chemical and crystalline phases and the film hardnesses are discussed in relation to the substrate temperature and the ion beam assistance during deposition.

2. EXPERIMENTAL

The Ti/Si/C films were deposited from a pre-synthesized Ti_3SiC_2 MAX phase target [2] by pulsed laser deposition (PLD) with a Quantel Brilliant pulsed Nd:YAG laser (Quantel S.A., Les Ulis, France; wavelength = 1064 nm, pulse duration = 6 ns,

repetition rate f = 20 Hz). The energy density of the laser beam was set to 6 J/cm^2 and the deposition time for all experiments was 30 min. The Si (100) single crystal substrates were sputtercleaned by a 2 kV argon ion beam for 15 min prior to deposition. To prepare the stainless steel substrates, commercially available steel sheets of 1~mm thickness (AISI 314) were cut, subsequently ground with SiC grinding paper (mesh 500, 1200, 2400 and 4000) and finally polished with diamond slurry (6 and 3 µm) to a final mean roughness R_a = 15 nm. During deposition the substrates were heated by a resistance heater from the reverse side to temperatures ranging from room temperature to 650 °C. The temperature was measured by a NiCr-Ni (type K) thermocouple. Prior to deposition without the ion beam, the deposition chamber was evacuated to 10^{-5} Pa. The Ar ion beam (Ar 99,998 %, Air Liquide, Düsseldorf, Germany) was generated by a Tectra IonEtch sputter gun (Tectra GmbH, Frankfurt/M., Germany) under an angle of 45 ° towards the substrate surface with an Argon pressure of 5×10^{-2} Pa and a source current of 20 mA. The measured total beam current at the substrate holder (area = 875 mm²) was 8 µA. The films were grown to a total thickness of 100 nm to 600 nm, depending mainly on deposition temperature. A Siemens D5000 X-ray diffractometer (Siemens AG, Munich, Germany) utilizing Cu K-radiation was used for X-ray diffraction measurements. The scans were performed as 5 ° grazing incidence measurements from 25 to 75 ° with 0.02 ° increments, using time steps of 1 s per increment. The glow discharge optical emmision spectrometry was carried out on a GDA750 Glow Discharge Spectrometer (Spectruma GmbH, Hof, Germany) in DC mode (1000 V, 15 mA). For the XPS measurements a Phi Quantum 2000 with Al Kα radiation (ν = 1487 eV) was used. Since XPS only has an information depth of a few nanometers, the sample surfaces were sputtered with a 4 keV Ar ion-beam prior to the measurements. Hardness measurements were performed on a Fischerscope H100 nanoindentor with a force of 3 mN applied during indentation.

3. RESULTS AND DISCUSSION

3.1. GDOES-measurements

GDOES measurements for all samples show that the stoichiometric Ti_3SiC_2 composition (50 at.% Ti, 17 at.% Si and 33 at.% C) of the ablation target is not represented in the thin films. While the titanium content in the films is between 46 at.% and 56 at.%, there is only about 27-32 at.% carbon and even less silicon (about 7-12 at.%.). The remaining amount in the samples is oxygen ranging from about 3 at.% to 17 at.%. Figure 1 shows the GDOES measurement of the sample deposited on MgO at 650 °C. The film shows a homogeneous distribution of the elements with an oxygen content of about 3 at.%. The total elemental compositions of all samples depending on the deposition temperature are given in figures 2 (MgO substrates), 3 (silicon substrates) and 4 (stainless steel substrates). Data for the sample deposited at 650 °C on Si with the ion beam applied is missing, because the film did not stick to the substrate, tore and delaminated. As mentioned above, the composition of all samples differs from the desired Ti_3SiC_2 composition. This is mainly due to the incorporation of oxygen during deposition. Obviously, the residual oxygen content in the chamber during deposition was too high to prevent an oxidation of the films. When the chamber is flooded with argon to set the ion beam running an additional contamination with oxygen due to insufficient purity of the argon gas is

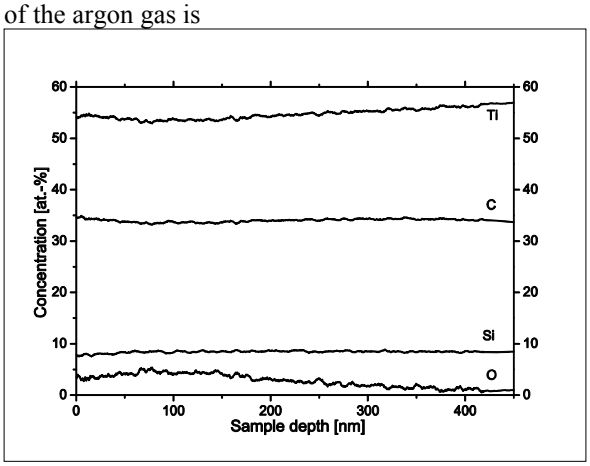

Figure 1: GDOES measurement of the sample deposited on MgO at 650 °C without ion beam applied.

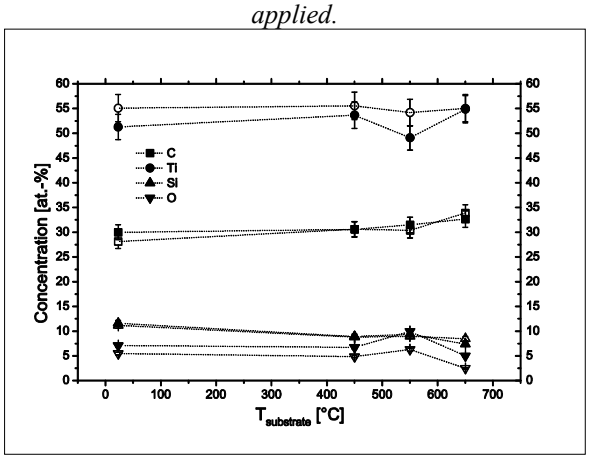

Figure 2: Overall elemental compositions of the films deposited on MgO(100). Open symbols: no ion beam, closed symbols: depositon with 200 V Ar ion beam. The lines are a guide to the eye only.

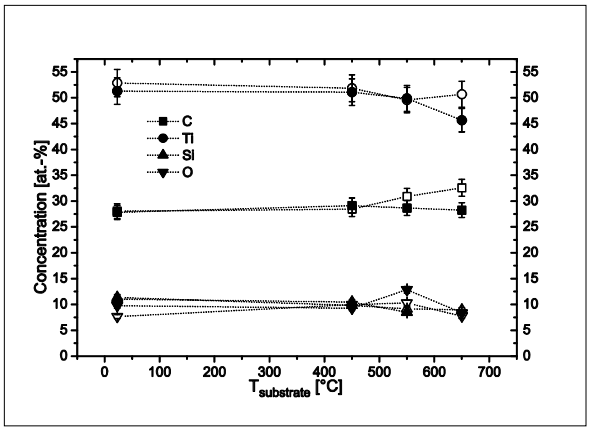

Figure 3: Overall elemental compositions of the films deposited on Si(100). Open symbols: no ion beam, closed symbols: depositon with 200 V Ar ion beam. The lines are a guide to the eye only.

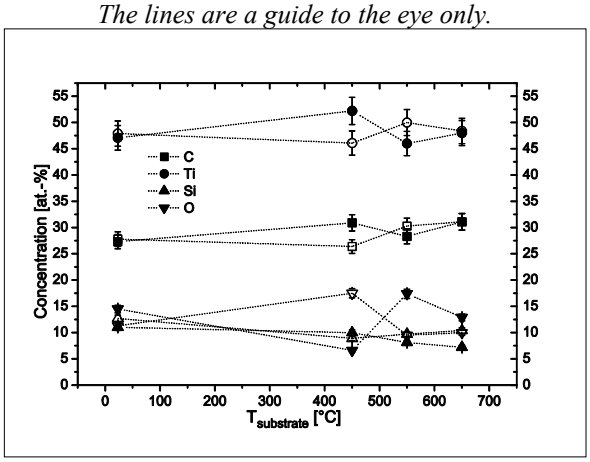

Figure 4: Overall elemental compositions of the films deposited on stainless steel. Open symbols: no ion beam, closed symbols: depositon with 200 V Ar ion beam. The lines are a guide to the eye only.

introduced to the experiment, which results in an increased oxygen take-up in the samples compared to those deposited in high vacuum. The XPS measurements described below show that the oxygen is bound to titanium and silicon as substoichiometric oxides TiO_x and SiO_x. On MgO, the oxygen content ranges from 3 to 10 at.%, on silicon from 5 to 13 at.% respectively. The samples deposited with the ion beam (closed symbols) have slightly higher oxygen content than those deposited in vacuum (open symbols). On the MgO and Si substrates the highest oxygen content is in the samples deposited at 550 °C, which will be discussed below. In the case of the stainless steel substrates the silicon and oxygen contents show a less stringent behaviour. Here, the overall oxygen content is even higher than on MgO and Si, varying from 7-17 at.%. Presumably the rather ill-defined surface of the stainless steel substrates plays a role in this additional oxidation. Since the substrates were no further treated after polishing, their surfaces are rougher than those of MgO and Si and they already contain various oxides (iron and chromium oxides) from the steel exposed to air. This additional oxygen can easily diffuse into the thin films during deposition. The fact that, when diffusion is intensified by applying the ion beam, the samples also contain even more oxygen approves this assumption.

The incorporation of oxygen is accompanied by a loss of silicon and carbon, while the titanium content remains essentially at about 50 at.%. This loss of silicon and carbon can easily explained by oxidation reactions of carbon and silicon. Carbon is lost due to gaseous carbon oxides CO and CO_2, silicon is lost due to the formation of volatile silicon monoxide SiO. It is noteworthy that although the oxygen content increases with increasing substrate temperature, because of a higher oxidation rate, the highest oxygen content is not found in the samples grown at 650 °C but in those deposited at 550 °C. On the other hand the titanium content has a local minimum at 550 °C, and the silicon content is minimal at 650 °C. Obviously the oxidation of titanium is most efficient at 550 °C. Whereas at 650 °C even more silicon is lost from the sample, probably due to a reduction of silicon dioxide SiO_2 in the film to the volatile silicon monoxide SiO.

3.2. X-ray diffraction measurement (XRD)

The only crystallographic phase that can be identified in the samples is cubic titanium carbide TiC. The extent to which the corresponding reflections appear depends solely on the substrate temperature during deposition. Even at room temperature there are (quite broad) reflections of TiC(200). At higher deposition temperatures other reflections, namely TiC(111) and TiC(220) appear. Furthermore the overall intensities increase and the full widths at half maximum (FWHM) decrease, indicating an increasing crystallinity of TiC with bigger crystallites. The x-ray diffractograms of films deposited without ion beam at 650 °C are given in figure 5. Overall the degree of crystallinity of TiC on the stainless steel substrates is smaller than on MgO and Si as can be seen from the less pronounced reflections. From these results it can be concluded that titanium and carbon form TiC in the films and the cystallites are growing with increasing substrate temperature. The rather rough surface of the stainless steel substrates and the resulting diffusion processes at the substrate/film interface which lead to a higher oxidation also partially impede the crystallization of TiC, giving less distinct reflections of TiC in the X-ray diffractograms. These results are in agreement with magnetron thin film experiments in the Ti-Si-C system, where below a substrate temperature of 800 °C the samples were either amorphous or consisted of a crystalline TiC matrix with noncrystalline silicon embedded [5,11].

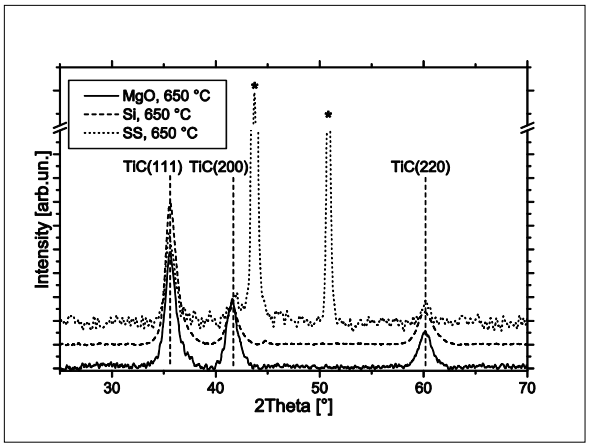

Figure 5: X-ray diffractograms of films deposited at 650 °C without ion beam. The reflections marked with an asterisk are γ-Fe from the stainless steel substrates.

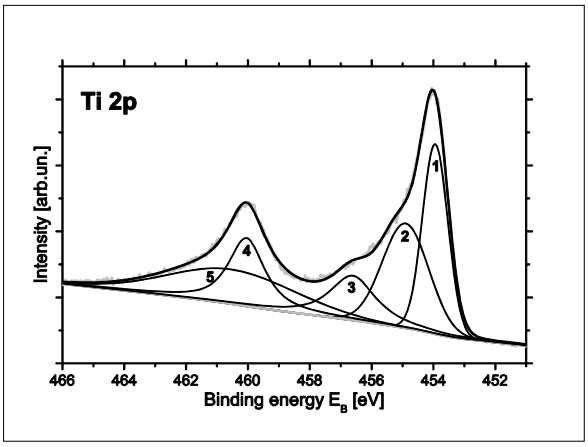

Figure 6: Deconvolution of the XPS spectrum at the Ti 2p core level into five spectral lines. The grey lines show raw data and background.

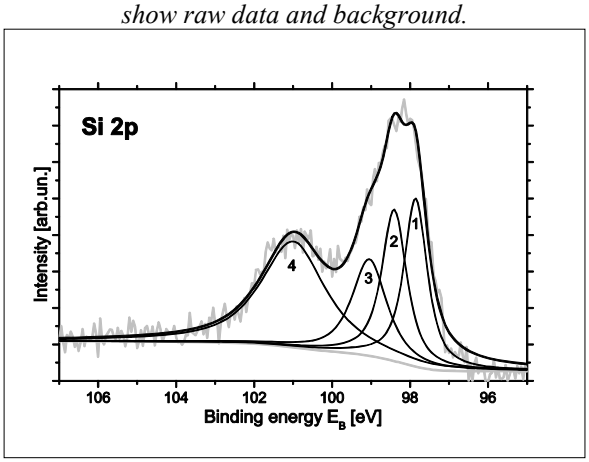

Figure 7: Deconvolution of the XPS spectrum at the Si 2p core level into four spectral lines. The grey lines show raw data and background.

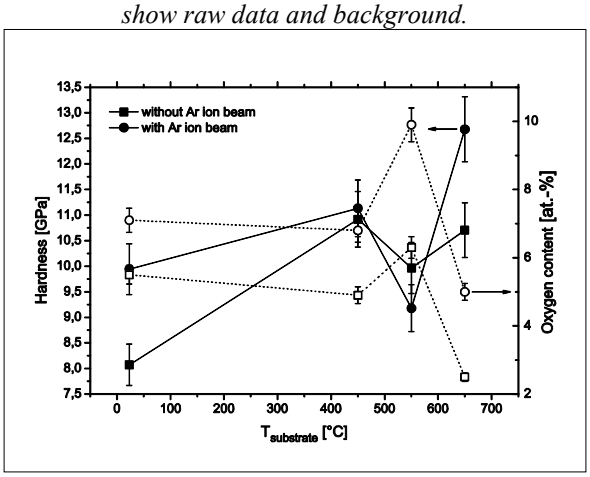

Figure 8: Hardness values (closed symbols, solid lines) and oxygen content (open symbols, dotted lines) of all samples deposited on MgO(100). The lines are a guide to the eye only.

3.3. XPS measurements

In order to gather more specific information about the chemical environments of the elements, XPS measurements on the Ti 2p, Si 2p and C 1s core levels were performed. The resulting spectra were deconvoluted using the "XPSPeak 4.1" software package. For the identification of the spectral lines the NIST XPS Database of the National Institute of Standards and Technology was used [12]. Figures 6 and 7 show the Ti 2p (EB = 451-466 eV) and Si 2p spectra respectively of a sample deposited at room temperature on Si(100). The Ti spectrum was deconvoluted into five spectral lines, which were related to the following chemical bonds: (1) EB = 454,0 eV: Ti 2p(3/2) in Ti, (2) EB = 454,9 eV: Ti 2p(3/2) in TiC, (3) EB = 456,6 eV: Ti 2p(3/2) in TiO1.5, (4) EB = 460,0 eV: Ti 2p(3/2) in Ti/TiOx and (5) EB = 460,5 eV: Ti 2p(3/2) in TiO. The Si spectrum was deconvoluted into four spectral lines. However, in this case a clear identification was not always possible. Unambiguously attributed were the lines (2) EB = 98.4 eV: Si 2p(3/2) in Si, (3) EB = 99.0 eV: Si 2p in Si/SiO_x and (4) EB = 101.0 eV: Si 2p(3/2) in SiC. For the value of line (1) EB = 97.9 eV no database entry was found. Given the binding energy of pure silicon (EB = 98.4 eV) which is closest to the value of line (1) it might be a distorted Si line due to the ion beam damage during pre-sputtering. Further investigations on the possible influence of the ion beam damage on the XPS spectra are currently carried out. The spectrum of the C 1s level (not shown here) consists of three spectral lines that can be assigned to TiC and SiC respectively. Thus, in addition to the crystalline TiC phase the samples also contain X-ray amorphous phases of titanium, silicon, silicon carbide, titanium oxide TiO_x and silicon oxide SiO_x.

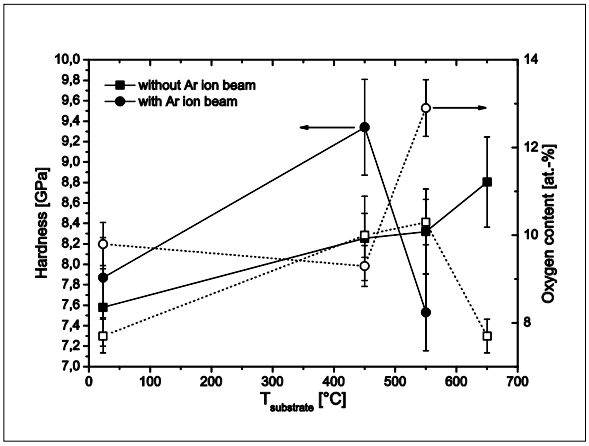

Figure 9: Hardness values (closed symbols, solid lines) and oxygen content (open symbols, dotted lines) of all samples deposited on Si(100). The lines are a guide to the eye only.

3.4. Hardness measurements

Hardness measurements were performed on the MgO and Si samples. The films deposited on stainless steel were too thin (about 100 nm) for a sensible hardness measurement. The values for all measured hardnesses are given in figures 8 (MgO substrates) and 9 (Si substrates). Again the data for 650 °C Si ion beam sample is omitted, because the film did not stick to the substrate. In general film deposited with the Ar ion beam apllied are slightly harder than the films grown without ion beam and hardness increases with increasing substrate temperature during deposition, which can be explained by the increased crystallinity of the TiC phase. The hardnesses on MgO substrates range from 8000 to 13000 N/mm^2, whereas the hardnesses on the Si substrates vary between 7500 and 9400 N/mm^2. The hardnesses of the MgO and Si substrates were measured for comparison, giving (10100 ± 500) N/mm^2 for MgO and (6900 ± 300) N/mm^2 respectively. There is however another important influence on the film hardness, namely the oxygen content. Figures 8 and 9 also show the oxygen content of the films, and it can clearly be seen that the hardness of the coatings correlates with the oxygen content. A higher atomic fraction of oxygen leads to lower film hardness and vice versa. The crystalline TiC matrix that gives rise to the quite high hardness values is disturbed by oxidized regions of SiO_x/TiO_x in between the TiC domains. The more of these oxides are in the film, the higher the disturbances and consequently the lower the total hardness of the coatings.

4. CONCLUSIONS

Thin films containing Ti, Si, C were deposited by pulsed laser deposition from a pre-synthesized target with the MAX phase composition Ti_3SiC_2 on different substrates over a temperature range from room temperature to 650 °C. In none of the grown films the formation of the Ti_3SiC_2 MAX phase was clearly observed. The composition does not match the desired values of stoichiometric Ti_3SiC_2. Instead, there is a significant incorporation of oxygen with a subsequent loss of carbon and especially silicon due to oxidation reactions during deposition. X-ray diffraction mesaurements show that only the binary MX compound TiC forms as a crystallographic phase. In addition XPS measurements indicate the presence of pure titanium and silicon, silicon carbide and the substoichiometric oxides TiO_x and $SiOx_x$. All of these phases however are X-ray amorphous. Films deposited with the Ar ion beam applied are slightly harder than those deposited without ion beam. The oxidized phases TiO_x and SiO_x also disturb the crystalline matrix of TiC, thus influencing the hardness of the films by making the films softer with increasing oxygen content.

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